

Scientific Understanding of Non-Chromate Inhibitors for Coatings Applications

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Overview

- An inhibitor screening approach for corrosion resistant coatings applications.
- Evaluation of lanthanide, transition metal oxoanion, Zn^{2+} inhibitors.
- Assessment of what matters for good corrosion protection from inhibitor pigment additions.

The support SERDP and the DOD is gratefully acknowledged.

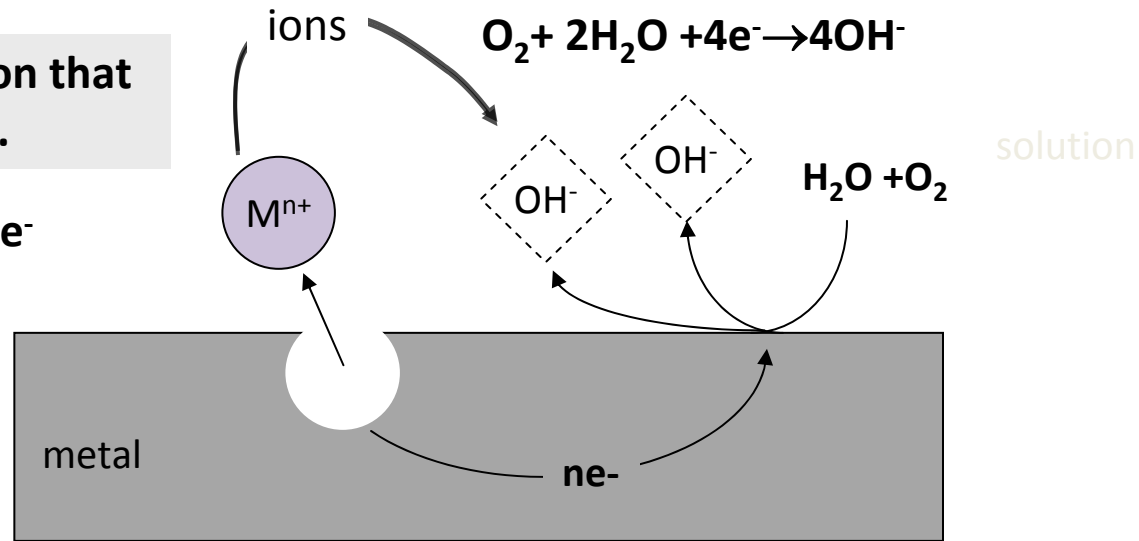
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Paired reduction-oxidation reactions constitute a corrosion reaction, otherwise known as a “corrosion cell”.

Oxidation: a reaction that produces electrons.



Reduction: a reaction that consumes electrons.



Reaction sites must be in electronic and ionic contact:

electronic - thru metal
ionic - thru solution

Chromate-Free Inhibitors in Current Organic Coatings

Inhibitor technologies used in state-of-the-art protective coatings

Material Characterized	Form	Active corrosion inhibitor
Cytec BR6700-1	Adhesive bond primer, cured film	Calcium silicate, zinc phosphate
Deft 02GN083	Paint primer, liquid resin	Praseodymium hydroxide,
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Deft 44GN098	Paint primer, liquid resin	Praseodymium hydroxide
Hentzen 16708/709	Paint primer, liquid resin	Calcium and magnesium silicate
Sherwin Williams cm0481968	Paint primer, liquid resin	Zinc oxide, aluminum phosphate
PPG RW-4057-64	Paint primer, liquid resin	Magnesium hydroxide
EcoTuff™	Inhibitive pigment	Cerous citrate, zinc molybdate

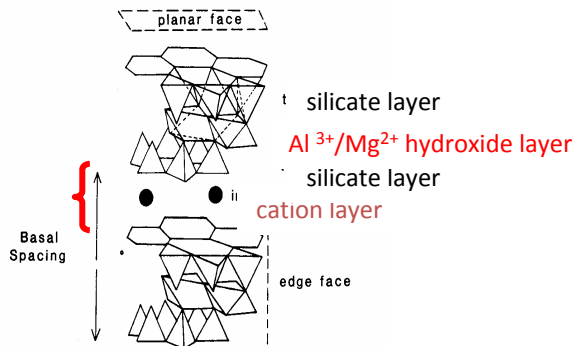
Based on these findings, model (reagent grade) inhibitor systems have been selected for solubility testing

The use of high capacity, synthetic ion exchange compounds as coating pigments is an approach for inhibitor delivery.

- Cationic clays (montmorillonites, bentonites)
Bohm et al., Werkst. u. Korros., 52, 896 (2001).



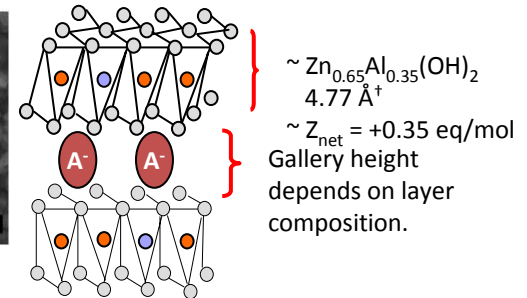
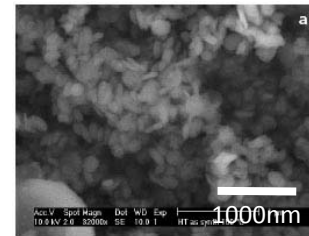
Huang, et al., J. Coll. & Interf. Sci. (2002).



Exchangeable cations:

Ce³⁺ **Pr³⁺**
Y³⁺ Tb³⁺
La³⁺
Zn²⁺

- Anionic clays (hydrotalcites).
Buchheit, et al., POC, 47, 174 (2003).



○ - OH
● - Zn
● - Al

Hosts:

$\text{Li}_2[\text{Al}(\text{OH})_3]_2^+$
 $\text{Ni}[\text{Al}(\text{OH})_3]_2^{2+}$
 $\text{Zn}[\text{Al}(\text{OH})_3]_2^{2+}$
 $\text{Mg}[\text{Al}(\text{OH})_3]_2^{2+}$

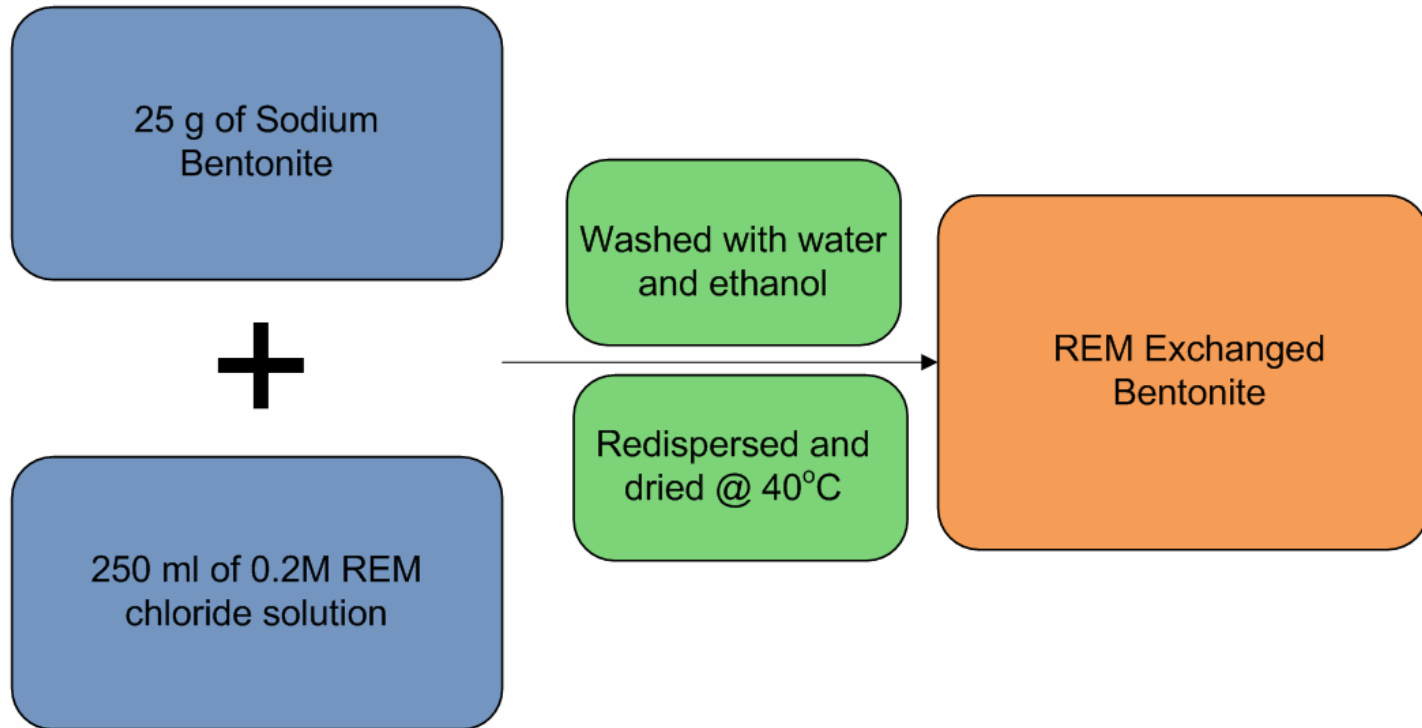
Exchangeable Anions:

CO_3^{2-}
 PO_4^{3-}
 SiO_3^-
 MoO_4^{2-}
 $\text{V}_{10}\text{O}_{28}^{6-}$

Approaches

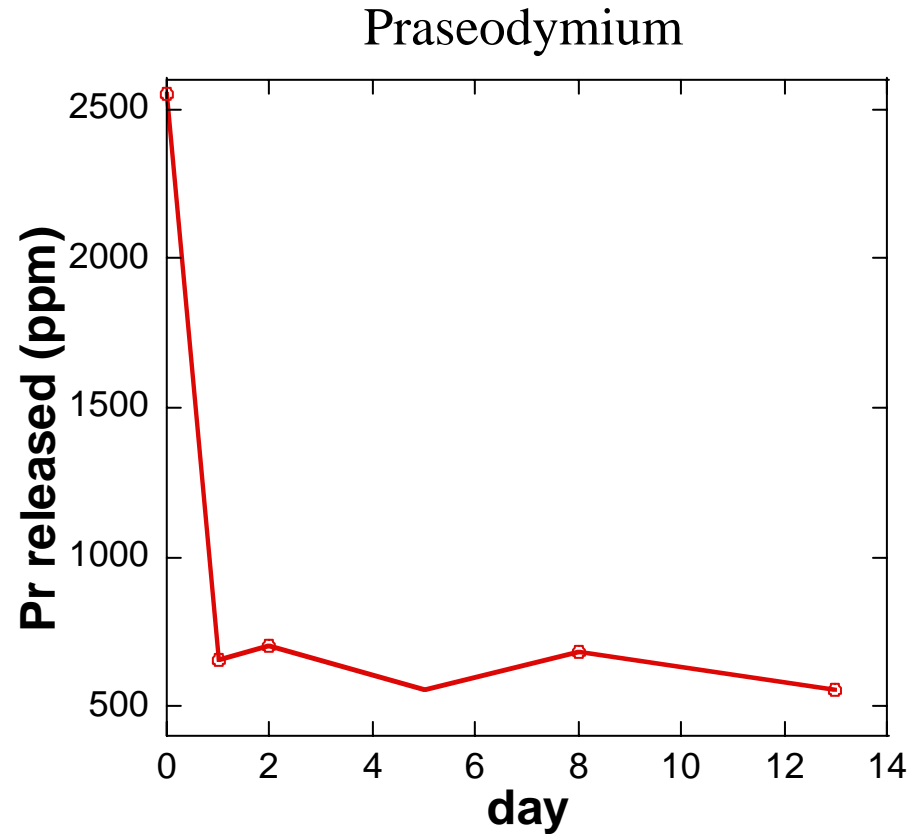
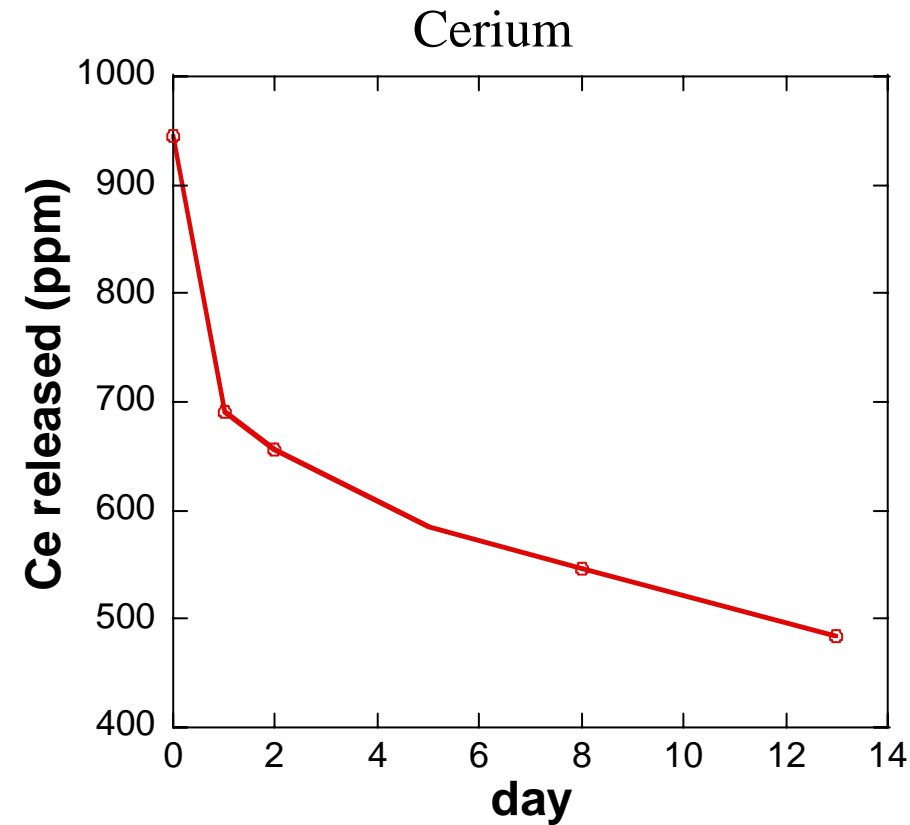
- Exchange anions: transition metal oxoanions for Cl^- or SO_4^{2-} in solution.
- Exchange cations: transition metal cations for Na^+ or K^+ in solution.
- Exchange both cations and anions using amphoteric exchangers or mixtures of clays.

Bentonite preparation.



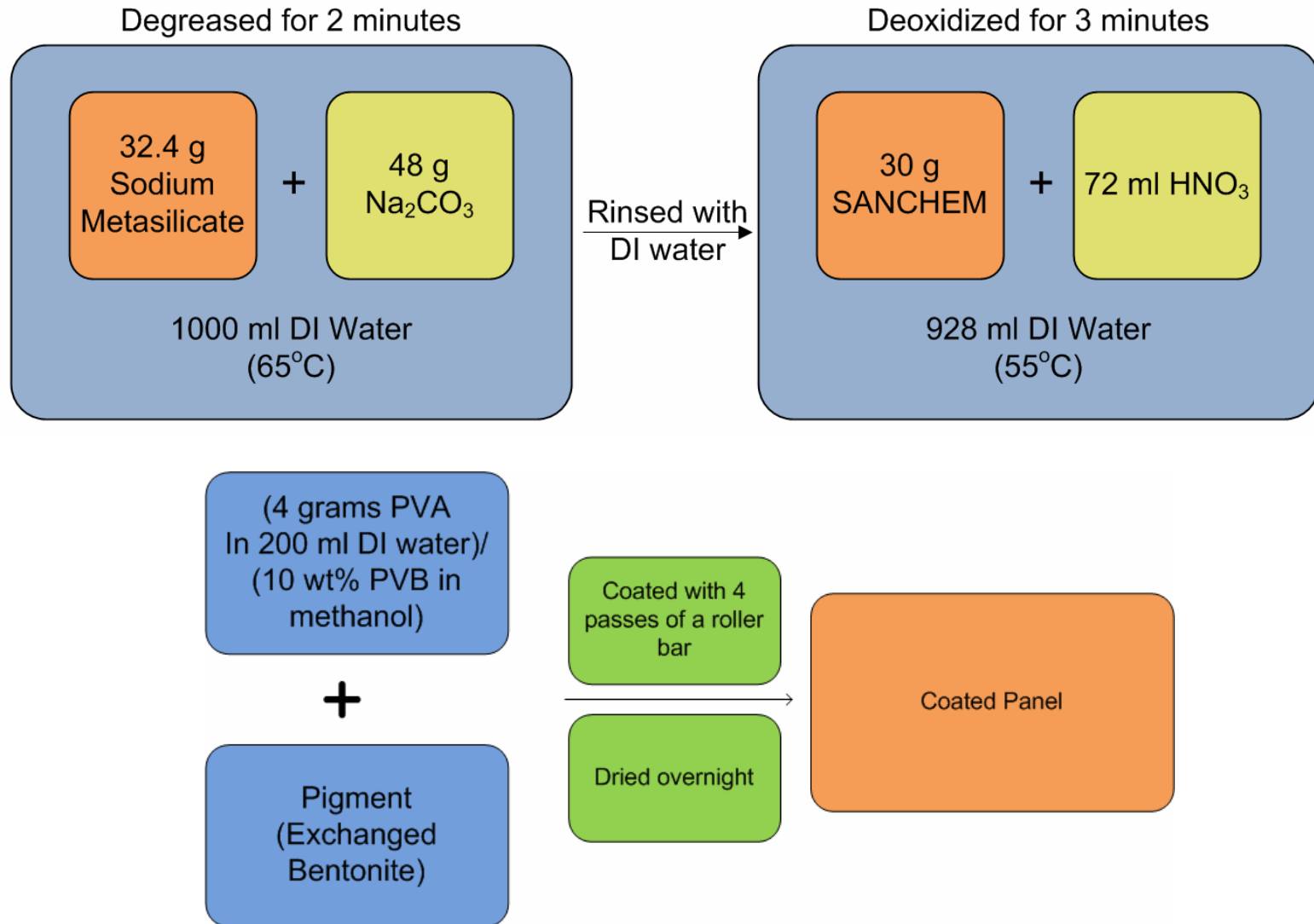
Exchanged cation release is tracked using UV-Visible spectra of 0.5M NaCl solution in contact with the REM bentonite

Inhibitor release from exchanged bentonites.

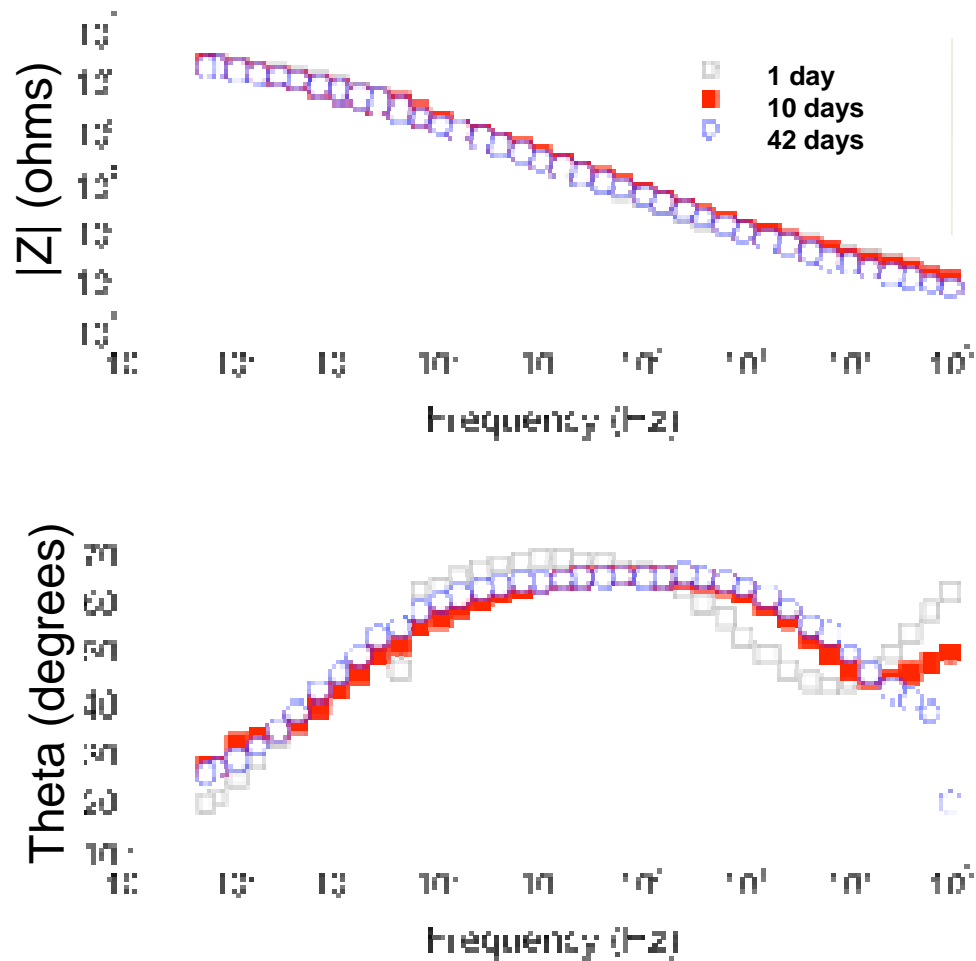


Inhibitor release from pigment slurries in a serial washing experiment.

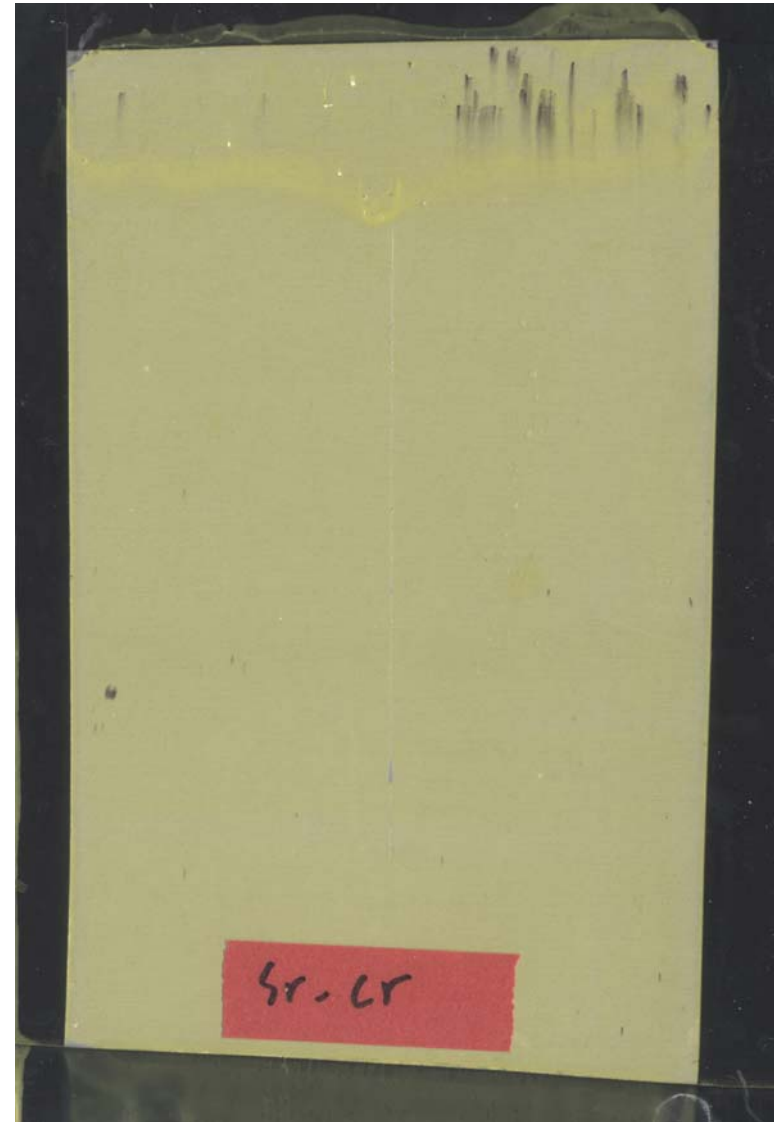
Preparation of substrate AA2024-T3 and PVA/PVB coatings.



Strontium chromate-pigmented positive control.

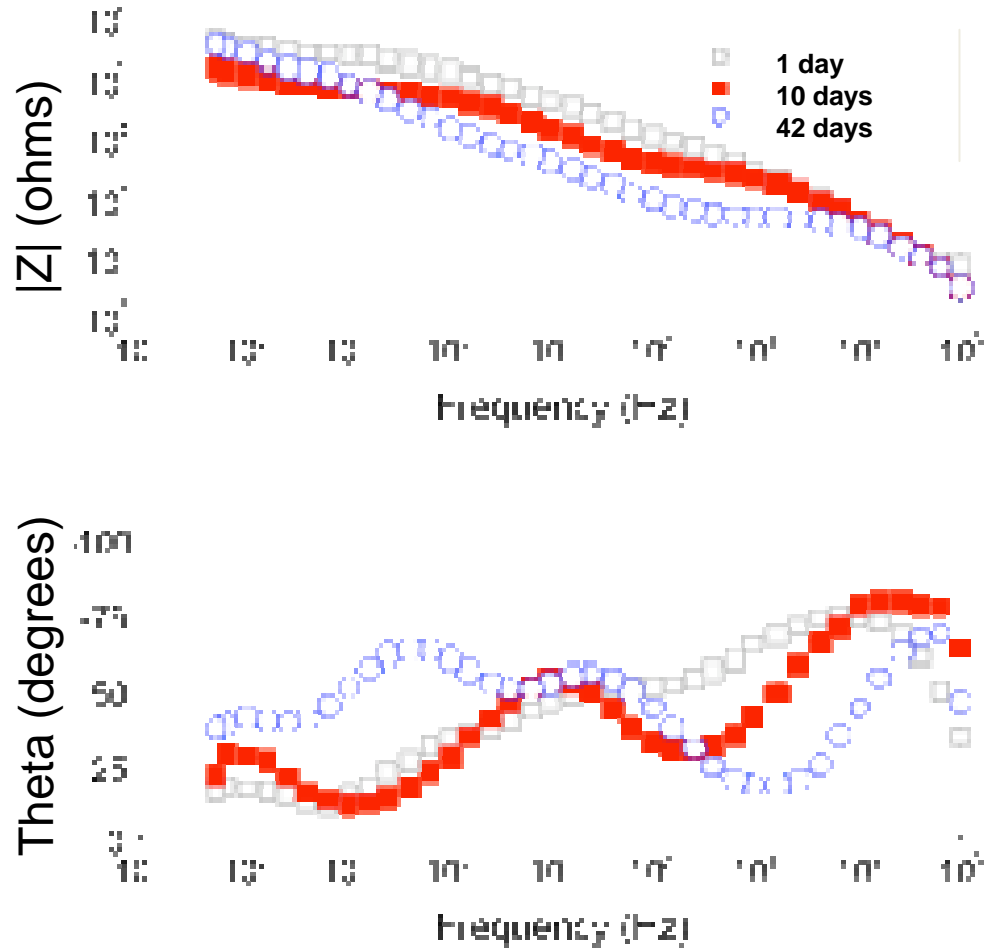


Cathodic inhibition by chromate adsorption and reduction.



1000 h SS exposure

PVB neat resin negative control.



Protection by barrier properties.



1000 h SS exposure

Scribed 2024-T3 panels after 1000 hours ASTM B117 Salt Spray Exposure. (5 wt.% pigment in PVB).



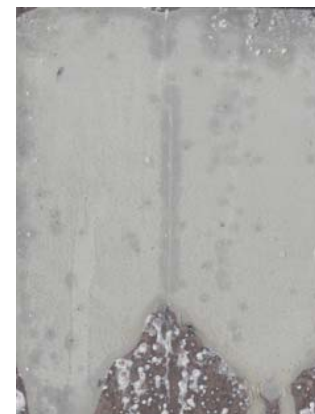
Neat



35ppm Ce^{3+}
89ppm Zn^{2+}
<1ppm PO_4^{3-}



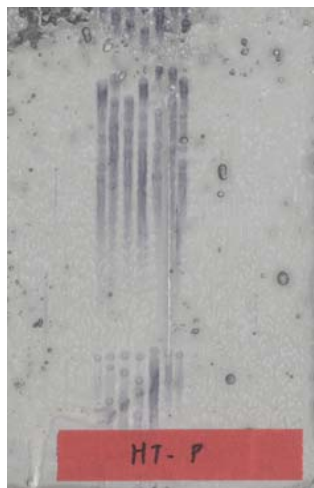
347 ppm Zn^{2+}



132ppm Zn^{2+}
<1ppm PO_4^{3-}
146ppm MoO_4^{2-}



Strontium
Chromate



10 ppm PO_4^{3-}



53 ppm Ce^{3+}
<1ppm PO_4^{3-}

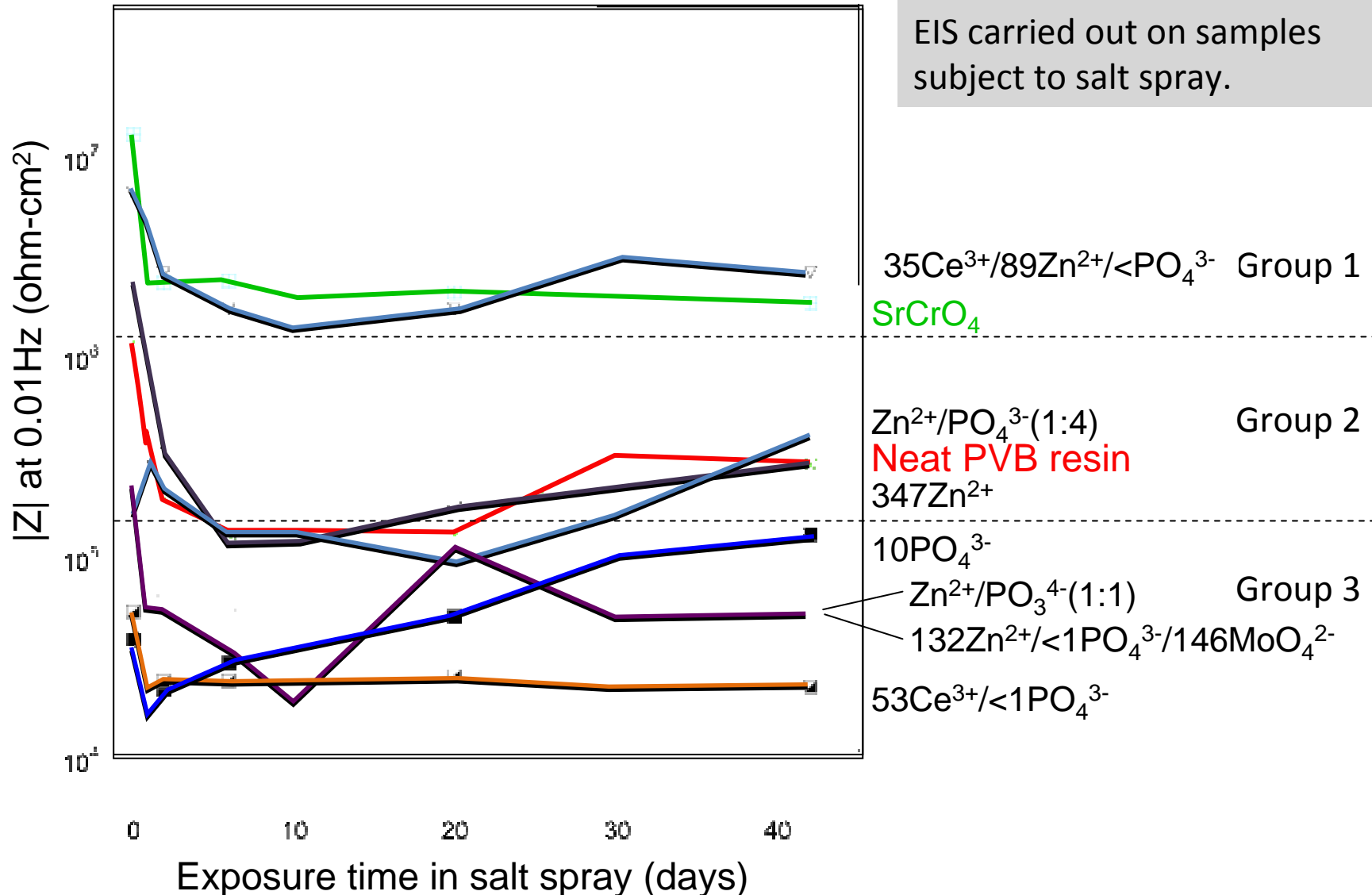


$\text{Zn}^{2+}/\text{PO}_4^{3-}$

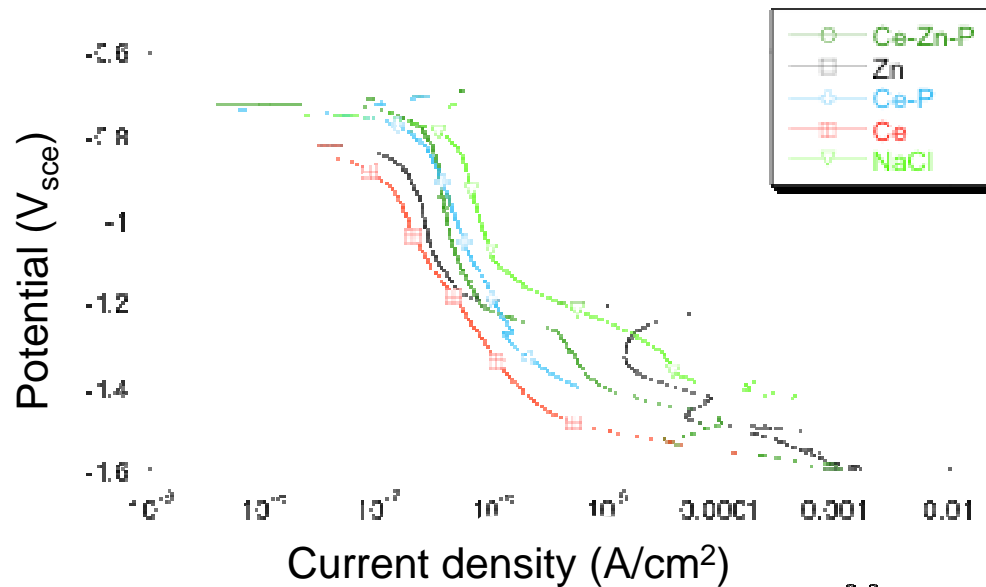


$\text{Zn}^{2+}/\text{PO}_4^{3-}$

Pigment screening using a total impedance metric allows the group of pigments to be broken into groups.

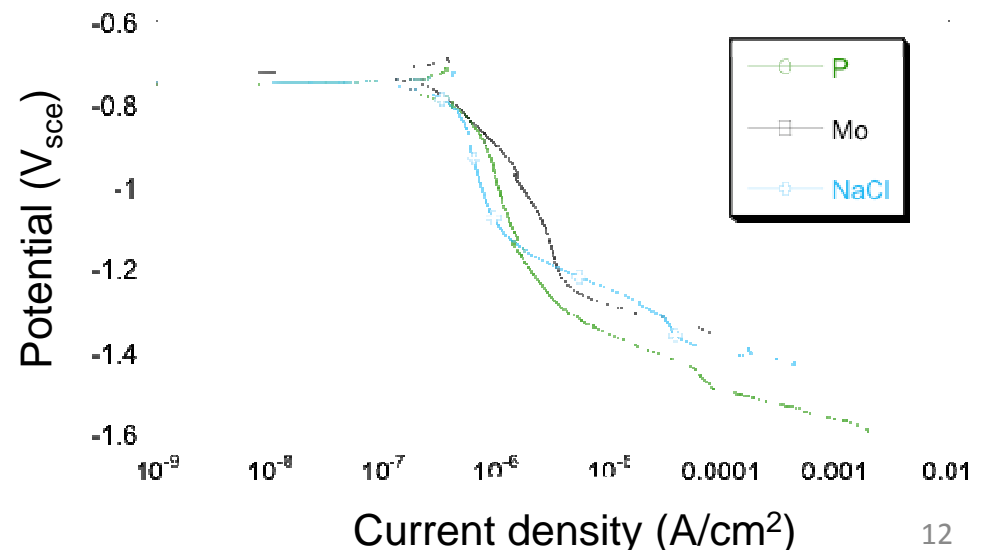


For coatings on Al alloys, high corrosion protection is strongly correlated with inhibition of oxygen reduction reaction

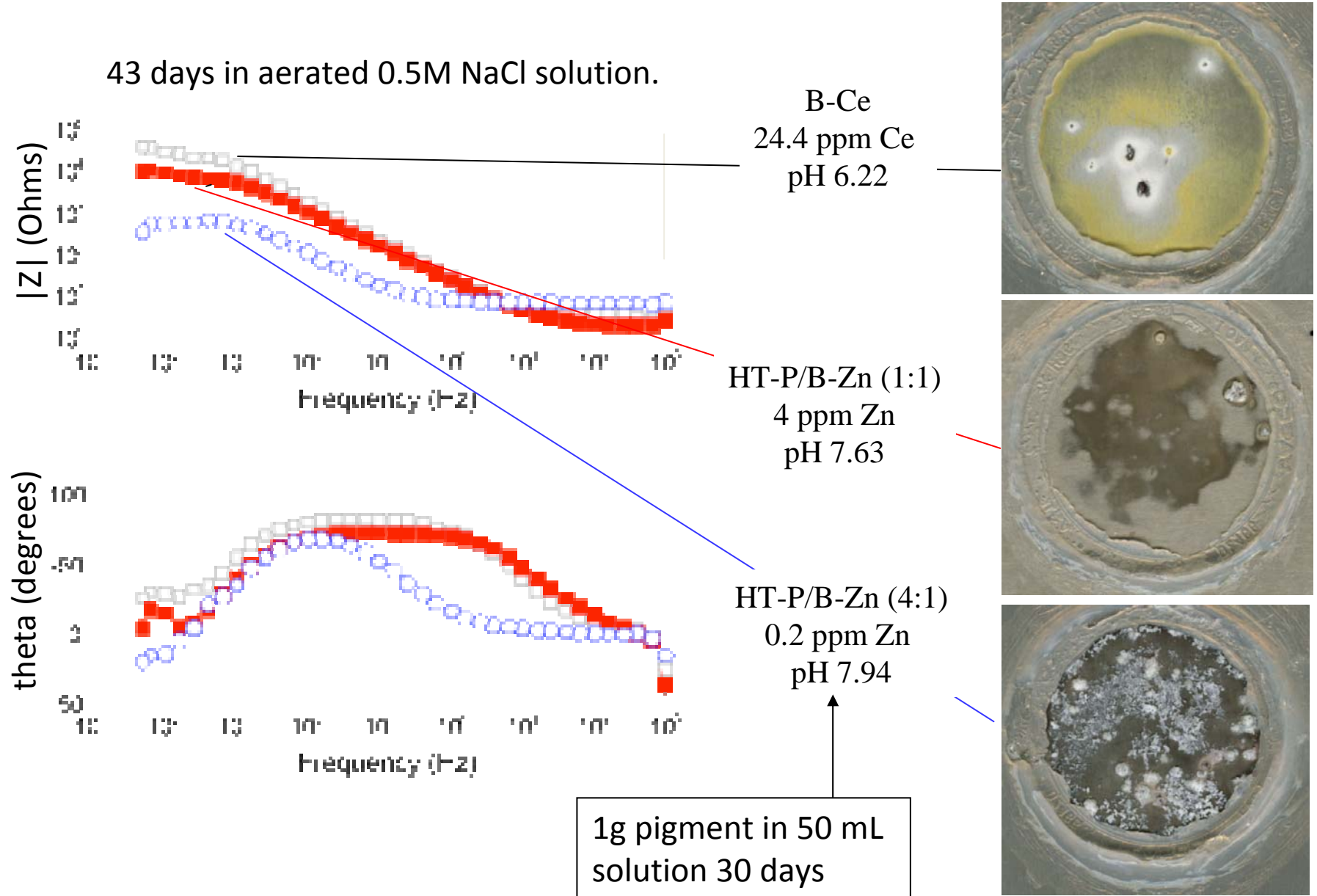


Ce^{3+} and Zn^{2+} are good cathodic inhibitors.

MoO_4^{2-} and phosphates are not.



In immersion experiments, coating corrosion protection scales with Ce or Zn dose.

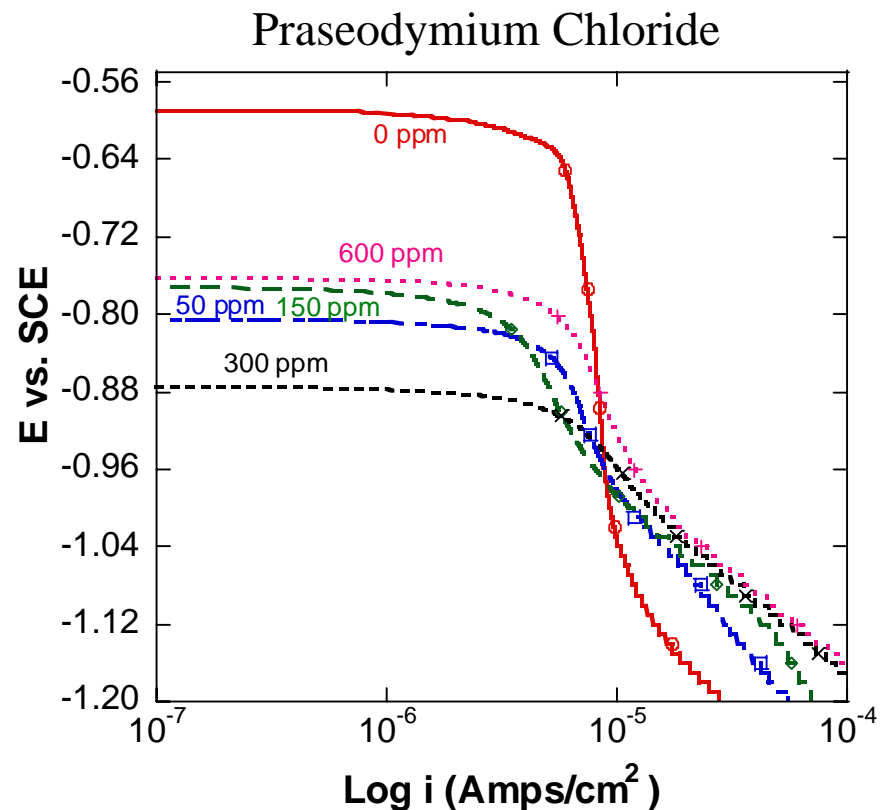
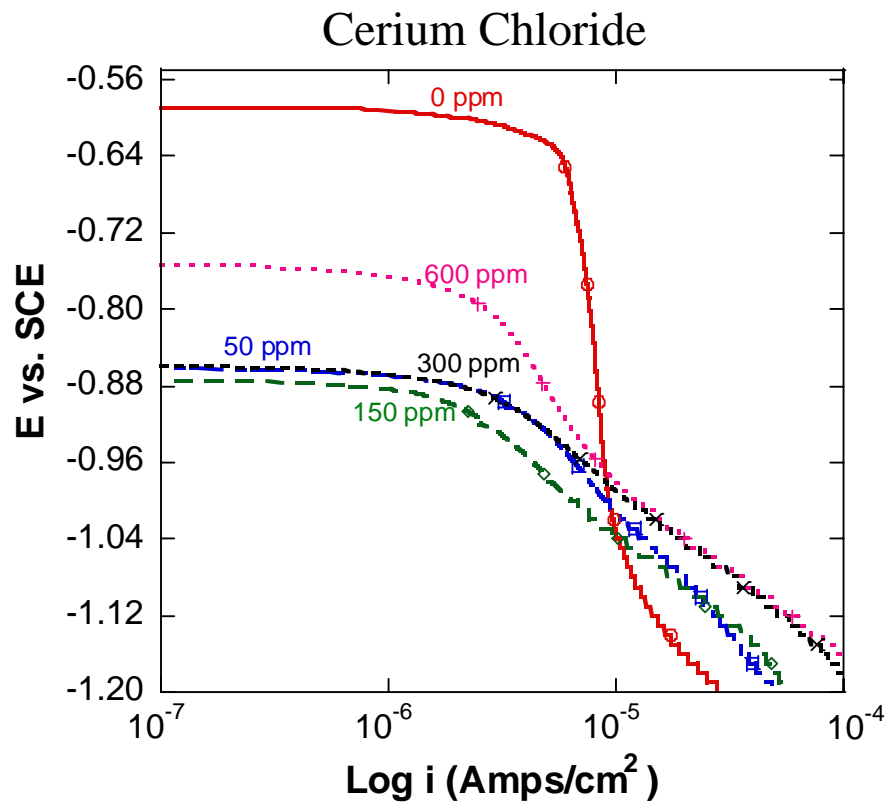


Some take-away points.

- The effectiveness of an inhibitor in a coating application correlates with its ability to inhibit the oxygen reduction reaction.
- Inhibitor effectiveness is concentration dependent.
 - critical minimum concentrations needed
 - critical concentration ranges may exist.
- Inhibitor effectiveness may depend on pH.

Lanthanides suppress oxygen reduction, but to varying extents.

Cathodic polarization on 2024-T3 substrates in aerated 0.1 M NaCl solution with chloride salts in various concentrations.



Free corrosion experiment and SEM analysis

The decreasing order of corrosion inhibition is Ce, Pr, La and Zn as inferred by inspection.



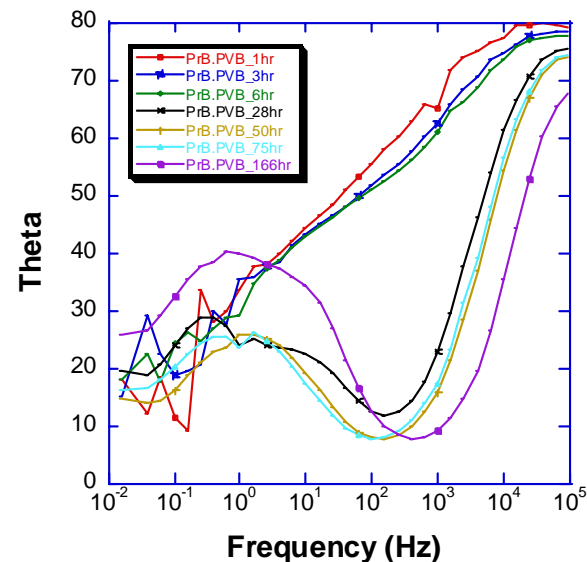
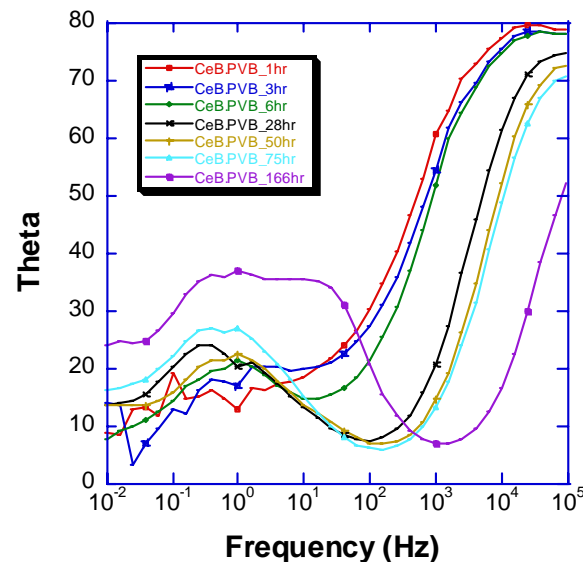
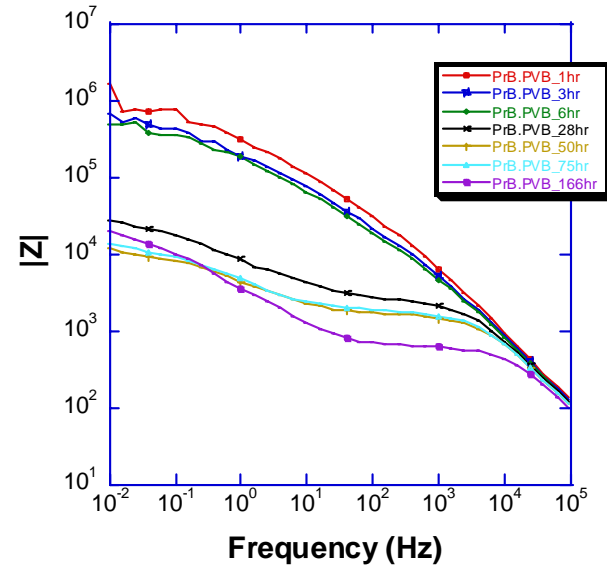
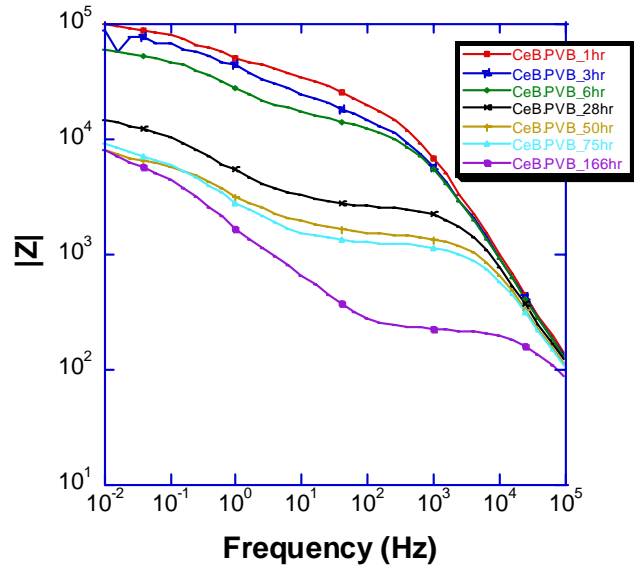
Ce

Pr

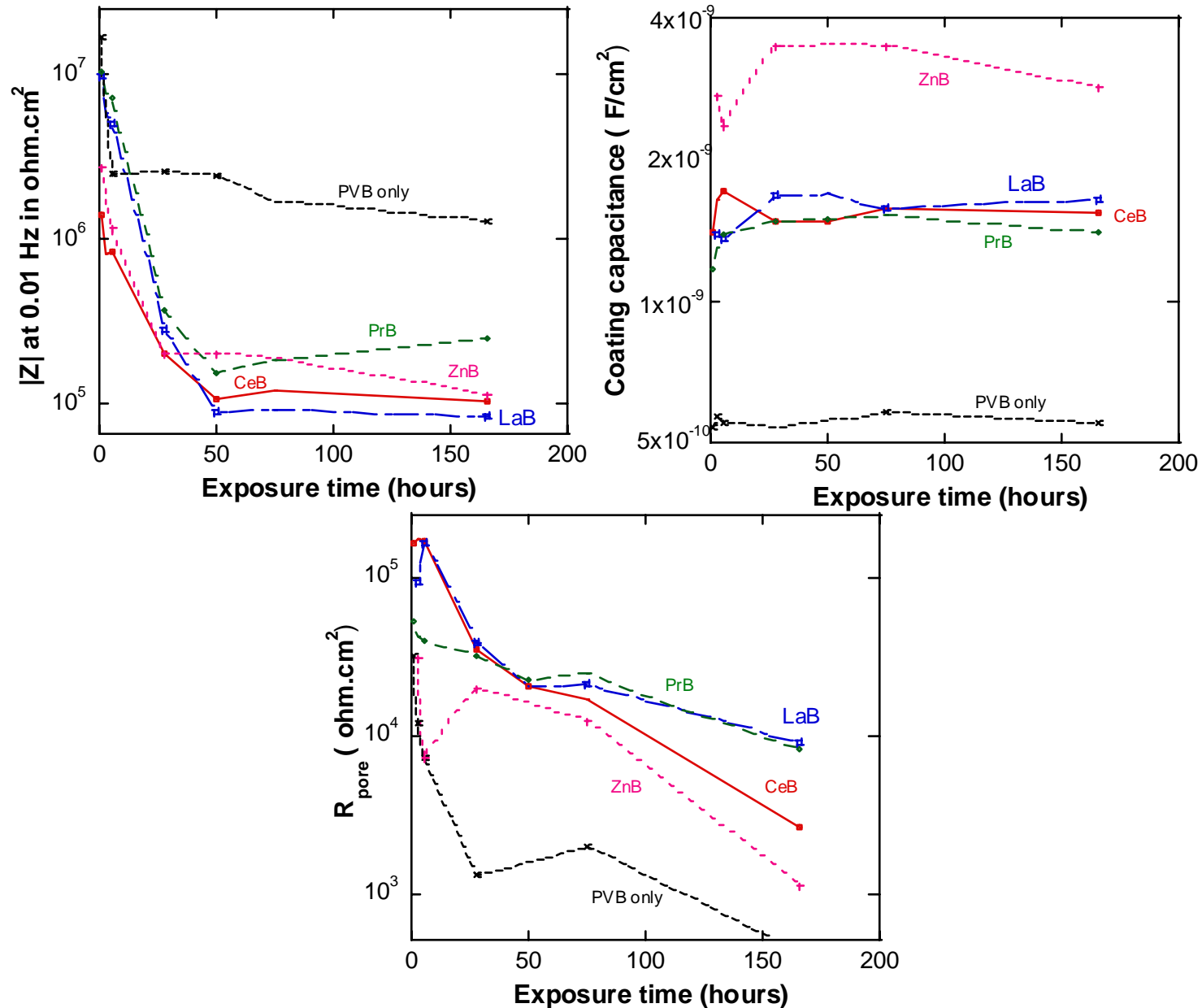
LaZn

- Al2024-T3 sample is immersed in solution of 100 mM NaCl solution and 300 ppm of the inhibitor (as a chloride salt) for 48 hours
- SEM, mapping and spot EDAX analysis was done to study the mechanism of inhibition

Time-dependent EIS for PVB coatings with 10 wt.% Ce^{3+} - and Pr^{3+} -exchanged bentonites on 2024-T3



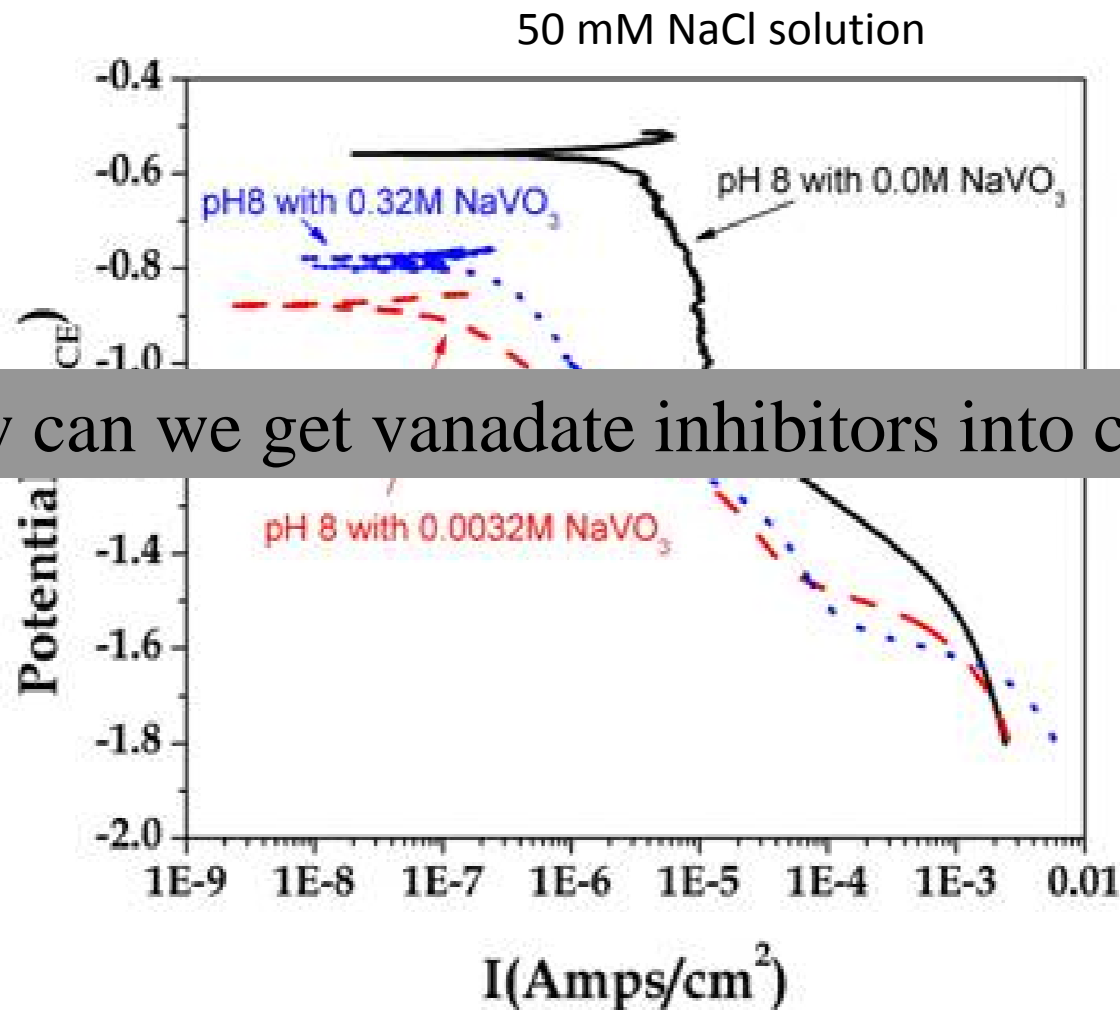
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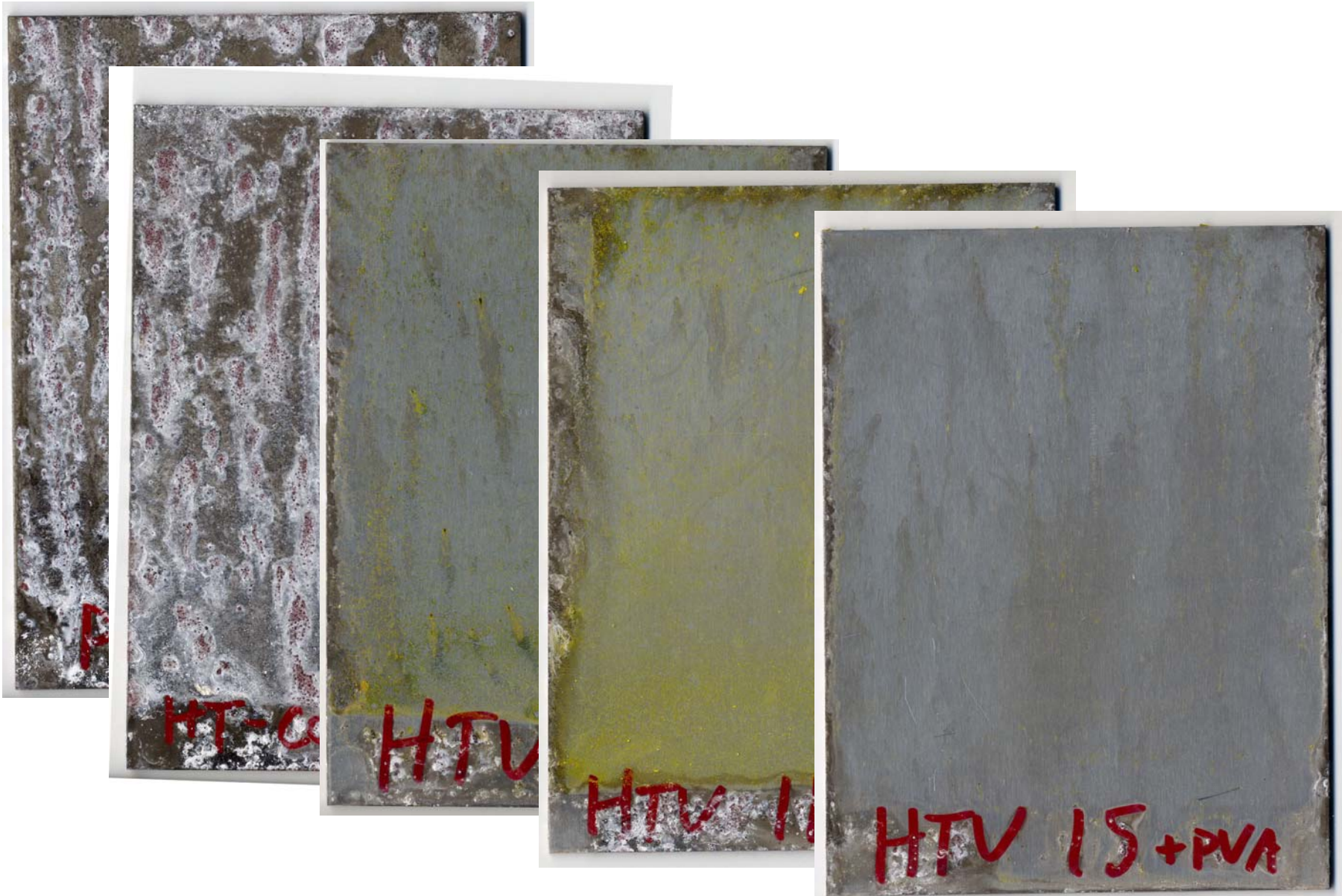
Some take-away points.

- Ce^{3+} and Pr^{3+} inhibit oxygen reduction to a similar extent, and protect to a similar degree in our screening experiments.
- Zn^{2+} is an intriguing, but inconsistent inhibitor for Al alloys in our experiments.
- None of the lanthanides or Zn^{2+} inhibit the ORR as effectively as chromate and corrosion protection in coatings where these inhibitors are present scale accordingly in our experiments.

Vanadates are potent inhibitors of oxygen reduction.



We use a rapid screening test to identify pigments for further development.



Rudimentary primers--epoxy plus IEC pigment give good scribe corrosion resistance.

1008 hours ASTM B117 salt spray exposure.



HT-V primer 25% loading
applied by drawdown bar
on silane pre-treated 2024-T3



HT-V primer 25% loading
applied by drawdown bar
on deoxidized 2024-T3

Summary--some answers to the core questions.

- What is the basis for selecting combinations?
 - Cathodic inhibition—specifically inhibition of oxygen reduction.
 - pH where effective.
 - Concentration where effective.
- What inhibitor combinations should be examined?
 - Focus on cathodic inhibition and account for substrate, environment, and transport.
- How are inhibitor combinations to be evaluated?
 - Electrochemical approaches for screening (hard to discriminate exposure results).
 - Exposure plus electrochemical approaches for evaluation.
- How are inhibitor combinations delivered?
 - Ion exchanging pigments and polymers.
 - Sparingly soluble salts (limited).
 - Triggered release (ICPs).

Pigments and pigment combinations

- Hydrotalcite pigments were synthesized by co-precipitation.
- Bentonite pigments were synthesized by ion exchange.
- Synthesis was verified by XRD.

Inhibitor concentrations developed by soaking 1g of pigment or pigment mixture in 50 mL 0.5M NaCl for 2 days



Anion exchangers

- Phosphate-bearing hydrotalcite HT-P
- Molybdate-bearing hydrotalcite HT-Mo

Cation exchangers

- Zinc-bearing bentonite B-Zn
- Cerium-bearing bentonite B-Ce

Mixtures

- Cerium and phosphate B-Ce + HT-P
- Cerium-zinc-phosphate B-Ce + B-Zn + HT-P
- Zinc-phosphate-molybdate B-Zn + HT-P + HT-Mo

Pigment corrosion protection is assessed in high permeability coatings.

Coating Application

- 5 wt. % pigment loading in polyvinyl butyral (PVB) (15 wt% in ethanol) on clean AA2024-T3
- Drawdown bar application; air cure.

Evaluations

- Salt spray exposure per ASTM B117 and periodic removal for EIS in 5% NaCl solution.
- Static immersion in aerated 0.5M NaCl solution.

Shift in the (001) peak in the sodium bentonite indicates cation exchange.

